

19) European Patent Office

11) Publication No.: 0 386 566
A 1

12)

EUROPEAN PATENT APPLICATION

21) Application No.: 90103648.3 51) International Cl.⁵:
22) Date of Application: 2/26/90 C11D 3/39, C11D 1/7230) Priority:
3/6/89 DE 390713171) Applicant:
Henkel Kommanditgesellschaft auf Aktien
Henkelstrasse 67
D-4000 Düsseldorf 13 (DE)43) Date of publication of the
Application: 9/12/90
Patentblatt 90/3772) Inventor:
Dr. Stefan Paasch
Lindener Strasse 9 H
D-3440 Wolfenbüttel (DE)84) Contracting states named:
GRInventor:
Jürgen Stodt
Hummelstrasse 24
D-4010 Hilden (DE)
Inventor:
Dr. Beatrix Kottwitz
Urdenbacher Allée 51
D-4000 Düsseldorf 13 (DE)

54) Title: Bleaching agent suspension

57) Abstract:

These are aqueous suspensions of solid peroxydicarboxylic acids, which contain a nonionic surfactant of the alcohol ethoxylate-type with an HLB value between 6 and 11. The suspensions excel by their high chemical and physical stability.

Translated from German by:
Quest Technology, Inc.
1603 S. Highland Avenue
Arlington Heights, IL 60005
(708) 439-4312
File No. QU0389

Bleaching agent suspension

The present invention belongs to the area of oxidizing and bleaching agents and refers to aqueous suspensions of peroxy-carboxylic acids.

Peroxycarboxylic acids, also called percarboxylic acids or peracids, represent very effective oxidizing agents and therefore these compounds have been proposed early as bleaching agents, disinfectants or for other purposes of oxidation. However, frequently, practical application of these compounds is thwarted by their low chemical stability, which is manifested by low storage stability and a tendency to explosive decomposition, especially in the pure form. Therefore, as a rule, percarboxylic acids are used together with stabilizing agents, with the aid of which one can reach sufficient stability for practical application. Examples of solid peracid formulations of this type are given in Belgian Patent 560 389, which is concerned with mixtures of percarboxylic acids and hydrates of inorganic salts. Examples of liquid preparations of peroxycarboxylic acids are given in German Offenlegungsschrift DE 26 12 587 in the form of suspensions of water-insoluble peracids in an aqueous liquid, the viscosity of which was increased with a polymeric thickener. European Offenlegungsschriffts 160 342, 176 124, 201 958 and 240 481 describe suspensions of water-insoluble peroxy-carboxylic acids in aqueous anionic surfactant solutions which are thickened with inorganic salts. In principle, the suspension form is a convenient manageable form of percarboxylic acids. However, in practice, difficulties arose, not only due to the lack of chemical stability of the peroxy-carboxylic acids, which is manifested by the self-decomposition that occurs at various rates of the compounds, or by interaction with the other components of the suspension, but also by difficulties which are to be attributed to a lack of physical stability. Practically all the percarboxylic acid suspensions that have been proposed so far and which are sufficiently liquid, tend to a sedimentation of the peroxy acid particles upon long standing with the consequence that the suspensions must be homogenized again before use and that, in the region of the

sediments, again the danger of exothermic self-decomposition exists. Therefore, the task was to provide possibilities for a more stable suspension of water-insoluble percarboxylic acids.

The object of the invention is a suspension of solid peroxy-carboxylic acids in an aqueous surfactant solution in which, as an essential component, an ethoxylate of a long-chain aliphatic alcohol with an HLB value between 6 and 11 is contained.

The suspensions according to the invention are characterized by extraordinary chemical and physical stability. A further essential advantage is the low viscosity of the suspensions, which is maintained even at high contents of suspended peracid. As an essential component, the suspensions according to the invention contain a certain type of nonionic surfactant: these are ethoxylates of long-chain aliphatic alcohols, whereby these alcohols preferably have 10 to 18 C-atoms and are preferably primary and/or unbranched. The ethoxylates are prepared in the known manner from ethylene oxide and alcohols in an addition reaction. The ethoxylates used according to the invention have an HLB value between 6 and 11, preferably between 7.5 and 10.5. This value, introduced by W. C. Griffin (Journal of the Society of Cosmetic Chemists, page 249 (1954)), is employed generally today for the classification of surfactants, especially of nonionic surfactants. Various methods are used for the determination of the HLB value of a surfactant, but, in the framework of this invention, the method of calculations proposed by W. C. Griffin for alcohol ethoxylates are used. Accordingly, the HLB value is determined according to the following formula:

$$\text{HLB} =$$

where E is the percentage by weight of the ethylene oxide content in the surfactant molecule.

Examples of nonionic surfactants that are suitable according to the invention are addition products of decanol and 2 to 4 moles of ethylene oxide (EO), addition products of dodecanol or tetradecanol and 2 to 5 moles of EO, addition products of hexadecanol and 3 to 6 moles of EO and addition products of octa-

decanol and 3 to 7 moles of EO. In practice, the ethoxylates are usually prepared from mixtures of long-chain alcohols and, in addition, they are present as mixtures of molecules with different degrees of ethoxylation: Therefore, in order to determine the HLB values, here the mean molecular weight (number-average) and the mean ethylene oxide content are used. The following will be named as examples of suitable technical nonionic surfactants:

name		alcohol basis		mole of EO	HLB
Dehydol ^R	LS2	C ₁₂ -C ₁₄	fatty alcohol	2	7.7
Dehydol ^R	LS3	C ₁₂ -C ₁₄	fatty alcohol	3	9.4
Dehydol ^R	LS4	C ₁₂ -C ₁₄	fatty alcohol	4	10.3
Dehydol ^R	LT2	C ₁₂ -C ₁₄	fatty alcohol	2	7
Dehydol ^R	LT3	C ₁₂ -C ₁₈	fatty alcohol	3	8.3
Dehydol ^R	LT4	C ₁₂ -C ₁₈	fatty alcohol	4	10
Dehydol ^R	TA5	C ₁₆ -C ₁₈	fatty alcohol	5	9.7
Dehydol ^R	TA6	C ₁₆ -C ₁₈	fatty alcohol	6	10.5
Dehydol ^R	D3	decyl alcohol		3	9.1
Lutensol ^R	AO3	C ₁₃ -C ₁₅	oxyalcohol	3	8.6
Lutensol ^R	AO4	C ₁₃ -C ₁₅	oxyalcohol	4	9.9
Dobanol ^R	25-3	C ₁₂ -C ₁₅	oxyalcohol	3	9
Dobanol ^R	25-4	C ₁₂ -C ₁₅	oxyalcohol	4	10.3

Naturally, mixtures of the individual technical surfactants with HLB values in the given range are also suitable.

Nonionic surfactants of the alcohol ethoxylate type are present in different phases in a mixture with water, depending on the concentration ratios and temperatures. Among others, we distinguish a lamellar liquid-crystalline phase, also called neat-phase in English, and a hexagonal liquid-crystalline phase, also called middle-phase (D. J. Mitchell et al., J. chem. Soc., Faraday Trans. 1, 79, 975 - 1000 (1983)). The occurrence of the individual phases can be followed by viscosity determinations and with the aid of a polarizing microscope and are usually plotted in the form of a phase diagram. Those nonionic surfactants of the alcohol ethoxylate type are especially suitable for application according to the invention, in which the melting point of the lamellar phase is higher than the melting point of the hexagonal phase. Melting point is defined as the highest temperature

at which the particular phase can still be observed. Especially preferred are those surfactants in which the melting point of the hexagonal phase is below 15°C.

Depending on the desired viscosity of the finished suspension, the concentration of the alcohol ethoxylate can be varied within wide limits. The viscosity of the suspension generally increases with the concentration of the nonionic surfactant and, if desired, can be taken to a pasty consistency. Therefore, preferably, the concentration of alcohol ethoxylate in the suspensions is between about 5 and about 30 weight percent, based on the total weight of the finished dispersion and the range from 5 to 20 weight percent is especially preferred. It is noteworthy that the suspensions have high physical stability even at relatively low viscosities.

In a special mode of execution of the invention, a part of the nonionic surfactants is replaced by surfactants of the betaine type. Betaine surfactants contain a quaternary ammonium group and an anionic group in the molecule, in addition to the hydrophobic portion. They are usually prepared by reacting long-chain tertiary amines, which preferably have a linear alkyl group having on the average 12 to 18 carbon atoms, by reaction with sultones, for example, propane sultone or, preferably by reaction with halogenocarboxylic acids, for example, chloroacetic acid.

Examples of such betaine surfactants are:

Dehyton^R AB 30;

Kokosalkyl-N* $(\text{CH}_3)_2\text{-CH}_2\text{-CO}_2^-$;

Dehyton^R K;

Kokosacyl-NH- $(\text{CH}_2)_3\text{-N}^*(\text{CH}_3)_2\text{-CH}_2\text{-CO}_2^-$.

With betaine surfactants, it is possible to use a lower total amount of surfactant in the suspension. In this connection, the effect of the betaine surfactant is exerted clearly, even at a weight ratio of betaine to nonionic surfactant of 1:10, but even more above a weight ratio of 1:4. One can regard the weight ratio of 4:1 as the upper limit, preferably 2:1 and especially 1:1. Depending on the amount of betaines in the surfactant mixture, it is possible to achieve good results in suspen-

sions with about 3 weight percent of this surfactant mixture as a total and, under certain circumstances, even with smaller amounts.

The peroxy carboxylic acids suspended according to the invention can be aromatic, aliphatic, alicyclic or heterocyclic percarboxylic acids, which are at least partly insoluble, and preferably are present in the insoluble form in an amount of more than 50% and especially in an amount more than 80%, in the aqueous suspension liquor at room temperature. Preferably, in the pure form, the percarboxylic acids should have a melting point above 50°C. Especially preferably, such peracids, which, even in the technical quality, that is, even when containing a significant percentage of the carboxylic acid on which they are based, are solid up to a temperature of 50°C. Among the percarboxylic acids named above, again, aliphatic compounds and particularly monopercarboxylic acids with 10 to 18 carbon atoms and alpha-omega-diperoxy carboxylic acids with 9 to 13 C atoms are especially preferred. Naturally, it is also possible to use individual compounds or mixtures of several peracids.

The amount of suspended peracid can be very high in the preparations according to the invention, so that, without an impermissible viscosity increase occurring, peracid contents of up to 30 weight percent and even higher can be reached in the suspension, based on the total weight of suspension, without any problem. Usually, peroxy acid concentrations up to 25 weight percent are used. The lower limit of the peracid content in the suspension is not critical and is determined mainly by economical factors. Peracid contents of more than 5, mostly more than 10 weight percent, based on the total weight of suspension, are customary, but, in special cases, significantly lower concentrations, for example, 1 or 2 weight percent can also come into consideration.

One can regard as another advantage of the preparations according to the invention that the particle size of the suspended peracid can be varied within wide limits without having a worsening of suspension stability. Particle sizes between about 1 and about 100 µm are customary, especially from 5 to 50 µm,

that is, in general, the percarboxylic acid can be suspended with the particle size that is obtained during synthesis.

In a further mode of execution of the invention, the suspensions contain additionally hydrogen peroxide, preferably in amounts between 0.1 and 20 weight %, especially between 2 and 15 weight %. This addition can contribute to the chemical stabilization of the peracids and, therefore, it yields a stronger action, especially when the suspensions are used as bleaching agent, especially at elevated temperatures.

In addition to the surfactants and percarboxylic acids as well as water, possibly hydrogen peroxide mentioned above, the dispersions may also contain auxiliary substances and additives, as long as these substances do not have an adverse influence on the stability. One should mention especially chelate complex-forming agents to make traces of heavy metal harmless; these substances may be contained in the dispersions in amounts of up to 2 weight percent, preferably 0.01-1 weight percent. One can use the usual complexing agents employed for the stabilization of peroxy carboxylic acids; however, preferably polyphosphonic acid is used, for example, 1-hydroxyethane-1,1-diphosphonic acid, or ethylenediaminetetramethylene phosphonic acid and their salts. As other optional components, one should mention inorganic salts as they are contained in technical products, resulting from the preparation of percarboxylic acids. The content of inorganic salts in the dispersions is preferably less than 1.5 weight percent, especially between 0.1 and 1 weight percent. Furthermore, one can add buffer substances to the suspensions in order to keep the pH value of the dispersions safely in the desired weakly acidic range, that is, in a pH value range between 1 and 7, preferably between 1.5 and 5. Anionic surfactants or cationic surfactants are not needed as additive in the dispersions, but they may be present in small amounts, as long as they do not have an adverse influence on the rheological properties of the dispersions and on the stability of the peracids. However, their amount must always be less than half of the other surfactants. As other additives, the peracid dispersions may contain dyes that are stable to oxidation, viscosity-regulating substances, for

example, polymeric carboxylic acids, such as polyacrylic acid or acrylic acid/maleic acid copolymers, hygroscopic substances and others. The total amount of auxiliary substances and additives in the dispersions is preferably not more than 10 weight percent and it is especially between 0.01 and 5 weight percent.

The preparation of the suspensions according to the invention presents no problems. The suspensions can be obtained without any special additives, by mixing the components and the sequence of addition can be chosen almost entirely arbitrarily.

When using powdered peracids, for example, first one can mix the suspension medium consisting of surfactant, water and possibly other components and then the peracid can be introduced. However, it is also possible to mix the peracid first with the other components and then stirring this mixture into water or into a solution of the remaining components in water.

In most cases, one does not start from pure percarboxylic acids, but from a premix that can be handled without danger, for example, such as obtained in the manufacture of percarboxylic acids. Such premixes contain about 10 to 95 weight percent of solid peroxy carboxylic acid in addition to water, but, they may also contain some of the carboxylic acid starting material (as a result of incomplete reaction during conversion into the peracid). Traces of hydrogen peroxide, mineral acid and inorganic salts, especially Na_2SO_4 and MgSO_4 may also be present. It should be considered a special advantage that, for the preparation of the dispersions according to the invention, these peracid premixes do not have to be dried, but can be used in the moist form as they are obtained in the production process.

Depending on the consistency, after the preparation, the dispersions are filled into bottles, cans or canisters but they can also be contained in tubes and other similar containers.

The dispersions according to the invention are preparations of peroxy carboxylic acids that can be handled easily and can be used in almost all cases instead of the solid percarboxylic acid preparations. In addition to use as oxidizing or disinfecting agents, the dispersions find application mainly as concentrated bleaches for hard surfaces and especially for textiles. For this

purpose, the dispersions can be used alone in a concentrated form or possibly after dilution, but it is frequently desirable to add the dispersions first to a treatment liquor which contains other further active ingredients, so that the bleaching or disinfecting action of the peracids can be used simultaneously with the actions that this treatment liquor exerts alone, in one treatment process. For bleaching or disinfection, the suspension is used preferably in such amounts that, in the solution that is used, the peracid concentration lies between 30 and 5000 ppm, especially between 100 and 2000 ppm. An especially preferred area of application for the peracid dispersions according to the invention is the addition of bleaching agent to washing liquors for the washing of textiles in the household and industry. Based on their consistency, the peracid suspensions are useful not only for manual dosage, but also for automatic dosage with the aid of suitable devices as they are preferred in the industrial area.

Examples

1. A technical alpha,omega-diperoxydodecanedioic acid (65.5 weight % peracid; 7.5% dodecanedioic acid; 27% water), 38.5 g, is introduced into a solution of 10 g Dehydol^R LS 4 (supplier Henkel, Düsseldorf) in 51.5 g of distilled water and the mixture was stirred with a blade stirrer at about 250 rpm for 30 minutes until complete homogeneous distribution was achieved. The viscosity of the suspension was 550 mPas (measured at 20°C with a rotary viscosimeter plate-plate measuring system with a 6 cm diameter and a 1000 µm gap width at a shearing rate of 50 s⁻¹). The pH value was 2.1.

For testing the stability, the suspension was stored at room temperature in glass bottles. The suspension was found to exhibit extraordinary physical stability. After 190 days, no sedimentation of the peracid particles and no sediment could be recognized visually. The chemical stability of the peracid was determined by potentiometric titration on a separately stored sample, always after prior homogenization. The content of the peracid decreased only very slowly and was

after days	weight % peracid
0	25
71	24
190	22

2. A suspension of 38.5 g of the technical peracid described in Example 1 was prepared in a solution of 4 g of Dehydol^R LS4 and 1 g of Dehyton^R AB30 in 56.5 g of water, using the method described in Example 1). The viscosity of the suspension was 240 mPas (measuring conditions as in Example 1). The pH value was 2.2.

The suspension also showed very good stability after 120 days of storage at room temperature, no sedimentation of the peracid particles and no bottom sediment could be detected. The peracid content (potentiometric) decreased only from 25 to 19 weight %.

Patent Claims

1. Suspension of solid peroxydicarboxylic acid in an aqueous surfactant solution, characterized by the fact that, as the essential component, it contains an ethoxylate of a long-chain aliphatic alcohol with an HLB value between 6 and 11.

2. Suspension according to Claim 1, in which the ethoxylated alcohol is chosen so that, in the phase diagram of the mixture of this surfactant with water, the melting point of the lamellar phase is higher than that of the hexagonal phase.

3. Suspension according to Claim 2, in which the melting point of the hexagonal phase is below 15°C.

4. Suspension according to Claim 1, containing 5 to 30 weight %, preferably 5 to 20 weight % of ethoxylated long-chain alcohol.

5. Suspension according to Claim 1, containing an ethoxylate of a primary, preferably unbranched alcohol with 10 to 18 C-

atoms.

6. Suspension according to one of Claims 1 to 5, in which the contained alcohol ethoxylate is replaced up to 45 [?], preferably 15 [?] to 12 [?] [no unit given], by a surfactant with betaine structure.

7. Suspension according to one of Claims 1 to 6, containing 1 to 30 weight %, preferably 5 to 25 weight % of solid peroxy-carboxylic acid.

8. Suspension according to Claim 7, which contains an alpha,omega-diperoxydicarboxylic acid with 9 to 13 C-atoms, preferably diperoxydodecanedioic acid as the peroxyacid.

9. Suspension according to one of Claims 1 to 8, containing 0.1 to 20 weight %, preferably 2 to 15 weight % of hydrogen peroxide.

10. Application of the suspension according to one of Claims 1 to 9, as oxidizing, bleaching or disinfecting agent.

11. Application according to Claim 10 as bleaching agent in washing liquors for textiles.

European Patent

Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 3648

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to Claim	Classification of the Application (Int. Cl. 5)
P,X	US-A-4 828 747 (M.E. REREK et al.) * Summary; column 1, line 7- column 2, lines 21, 48-63; column 3, line 14 - column 4, line 28; Example 1; Table I, D, G; Claims 1-3, 6, 7, 9, 14 *	1,4,5,7, 11	C 11 D 3/39 C 11 D 1/72
D,X	EP-A-0 160 341 (UNILEVER plc) * page 1, line 3 - page 6, line 34; page 7, line 20 - page 8, line 34; Example I; Claims 1-7, 9 *	1,4,5,7 8,10,11	

Technical fields searched (Int.Cl. 5)

C 11 D

The present search report has been drawn up
for all claims

Place of search: Date of completion of the search: Examiner:
THE HAGUE 4/26/1990 W.H.F.FISCHER

Category of cited documents:

- X: of special importance considered alone
- Y: of special importance considered in connection with another publication of the same category
- A: technological background
- O: nonwritten disclosure
- P: intermediate document
- T: theories or laws on which the invention is based
- E: older patent document which was published only on or after the date of application
- D: document cited in the application
- L: citation for other reasons
- &: member of the same patent family corresponding document